

The nature of an enhanced ferroelectric phase transition temperature in perovskite-based solid solutions

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We explain the phenomena of ferroelectric phase transition temperature T_c enhancement beyond the end members in perovskite solid solutions like $\text{BiMeO}_3\text{-PbTiO}_3$ (Me=Sc, In, etc.) is related to nonlinear and spatial correlation effects. The explanation is based on the calculation of T_c in the framework of our random field theory with additional account for nonlinear effects in the above substances. We show that the maximum of T_c for certain PbTiO_3 content takes place when coefficient of nonlinearity is positive, the value of this coefficient is found from best fit between theory and experiment. This nonlinearity coefficient is the only adjustable parameter of the theory. We show that enhancement of positive nonlinearity coefficients enhances greatly the T_c maximum over its value for end members.

The theory lays the foundation to calculate not only T_c for above solid solutions but virtually any equilibrium and/or nonequilibrium thermodynamic characteristics such as static and dynamic dielectric susceptibility, specific heat etc as a functions of PbTiO_3 content, temperature, electric field and other external parameters.

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I. INTRODUCTION

Over the last few years considerable effort has been spared to synthesize the dielectric materials with controllable properties for many technical applications. The most promising substances are believed to be the compound materials consisting of solid solutions of different combinations of ferroelectrics with different dielectric properties. One of the examples is perovskite solid solutions like $\text{BiMeO}_3\text{-PbTiO}_3$ (Me=Sc, In, etc.), which have high ferroelectric phase transition temperatures T_c at the morphotropic phase boundaries with enhancement beyond the end members. Such materials can be used as the materials with excellent high-temperature piezoelectric properties^{1,2,3,4,5,6}.

A common feature of the above solid solutions is the existence of numerous random fields sources due to substitutional disorder, unavoidable impurities, vacancies in anion and cation sublattices etc. These random fields play a crucial role in the properties of disordered ferroelectric and magnetic materials (see e.g.^{7,8,9}) and above substances in particular. This means that observable physical properties of above systems depend strongly on the form of random fields distribution function. Namely, the relation between width of the distribution function (the dispersion of random fields) and its first moment (mean value of random field) generates all observable features of the phase diagram of a disordered dielectric and/or magnetic materials, i.e. realization of ferroelectric (ferromagnetic in the case of magnetic materials) phase, dipole (spin) glass phase and mixed ferroglass phases. Also, so-called paraglass (Griffiths) phase may occur in

disordered dielectrics (see, e.g.¹⁰).

On the other hand, both ordered and disordered dielectrics have intrinsic nonlinearities, consisting in, e.g., dielectric hysteresis. The "interaction" between these nonlinearities and random fields lead to their renormalization so that the distribution function of random fields will also include a nonlinear contribution of random fields. Such calculation had been carried out in a different context in Ref.¹¹.

The calculations in Ref.¹¹ incorporate a self-consistent dependence of distribution function of random fields on the third order nonlinearity coefficient α_3 . It has been shown that when the nonlinear coefficient is sufficiently large and positive, the results are strongly different from those in linear case⁷. In particular, for $\alpha_3 > 0$, the phase transition temperature exceeds its mean field asymptotic value, while for $\alpha_3 < 0$ the results are qualitatively the same as in linear case. As we have found out earlier, this phenomenon is due to the "generation of order by disorder" (or more precisely, a specific positive feedback generated by positive nonlinearity) taking place at $\alpha_3 > 0$.

II. GENERAL FORMALISM

A. The distribution function of random fields

Here we briefly review the main facts about the shape of distribution function of random fields with respect to nonlinear effects, a more detailed discussion can be found, e.g. in Refs^{7,11} for disordered dielectrics and in Refs^{12,13}

for disordered magnetic semiconductors.

The distribution function of random field \vec{E} can be represented in the form

$$f(\vec{E}) = \overline{\langle \delta(\vec{E} - \vec{E}(\vec{r}_i)) \rangle} \quad (1)$$

Here the bar denotes averaging over spatial configurations of random fields sources (e.g. electric dipoles, "responsible" for emergence of ferroelectricity in the above compounds), $\langle \dots \rangle$ means the averaging over dipoles orientations, $\vec{E}(\vec{r}_i)$ is the internal electric field induced by electric dipoles and other sources in the observation point \vec{r}_i . In a disordered ferroelectric this field already contains the intrinsic nonlinearity and can be written in the form (see¹¹ for details)

$$E_\gamma(\vec{r}_i) = \mathcal{E}_\gamma(\vec{r}_i) + \sum_{m=2}^{\infty} \alpha_m \prod_{j=1}^m \mathcal{E}_{\gamma_j}(\vec{r}_i), \quad (2)$$

where $\gamma=x,y,z$ so that \mathcal{E}_γ denotes simply the γ component of vector $\vec{\mathcal{E}}$. Here $\vec{\mathcal{E}}$ is an internal electric field induced by electric dipoles, α_m is a coefficient of nonlinearity of m -th order. Note that the first term in Eq. (2) can be generalized to account for other possible sources of random fields such as point charges, elastic dipoles etc^{5,7,11}.

The calculation of the distribution function (1) with respect to (2) in the framework of statistical theory (see^{14,15} for details of this theory) for so-called disordered Ising model (when the dipole has only two admissible orientations) yields the following rigorous result for any electric field component $E_\alpha \equiv E$ ¹⁶

$$f(E) = \int_{-\infty}^{\infty} f_1(E') \delta \left(E - E' - \sum_{m=2}^{\infty} \alpha_m E'^m \right) dE' \quad (3)$$

where $f_1(E)$ is the distribution function, that takes into account only the first linear term in (2) (distribution function of the first order).

More detailed version of Eq. (3) reads

$$f(E) = \int_{-\infty}^{\infty} f_1(E') \times \times \delta \left(E - E' - \sum_{m=2}^{\infty} \alpha_m E'^m \right) dE', \quad (4)$$

$$f_1(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iEt - nF(t)} dt, \quad (5)$$

$$F(t) = \int d^3r \langle (1 - e^{-it\mathcal{E}(\vec{r})}) \rangle. \quad (6)$$

Here n and $\mathcal{E}(\vec{r})$ are the concentration and electric field of the dipoles. The Eq.(5) determines the function $f_1(E)$, calculated earlier in⁷ for the case of two-orientable electric dipoles. We note here, that in general case (e.g. arbitrary interaction between above dipoles, their arbitrary concentration etc, see Ref.⁷ and references therein for discussion) function $f_1(E)$ has non-Gaussian form. It can be shown that for our case of compound ferroelectrics it is sufficient to use its Gaussian asymptotics, which reads

$$f_1(E) = \frac{1}{2\sqrt{\pi n B}} \exp \left[-\frac{(E - E_0 L)^2}{4nB} \right]. \quad (7)$$

Here $L = \frac{\langle d^* \rangle}{d^*}$ and $E_0 = 4\pi(nd^{*2})/\varepsilon_0$ are the order parameter (number of coherently oriented impurity electric dipoles or dimensionless spontaneous polarization) and the mean value of random field of electric dipoles (in the energy units), $d^* = \frac{1}{3}d\gamma(\varepsilon_0 - 1)$ is the effective electric dipole moment, γ and ε_0 are, respectively, Lorentz factor and static dielectric permittivity of the host lattice, n is the concentration of electric dipoles. Coefficient B determines the width of the distribution function (dispersion of random fields) and depends on host lattice parameters like its correlation radius r_c , see⁷ for details.

B. The equation for long-range order parameter

In our approach, an average value \overline{A} of any physical quantity can be represented in the form

$$\overline{A} = \int_{-\infty}^{\infty} f(E) A(E) dE, \quad (8)$$

where $f(E)$ is determined by (4) and $A(E)$ is the above quantity for single random field constituent, averaged over its internal degrees of freedom. In our case this is the average value over the orientations of single electric dipole.

To calculate the T_c for disordered ferroelectric compound we need to calculate first the long-range order parameter L . In the spirit of Eq. (8) we obtain following self-consistent equation for this parameter

$$L = \int_{-\infty}^{\infty} f_1(E) \tanh \left[\left(E + \sum_{m=2}^{\infty} \alpha_m E^m \right) / kT \right] dE. \quad (9)$$

Here we use the fact that for two-orientable dipoles ($l_z = \pm 1$, $l_x = l_y = 0$) $A(E) = \langle l \rangle = \tanh(\frac{E}{kT})$, $E \equiv E_z$.

The self-consistency of Eq. (8) is revealed by substitution of Eq.(8) into it, which yields

$$L = \frac{1}{2\sqrt{\pi nB}} \int_{-\infty}^{\infty} \exp \left[-\frac{(E - E_0 L)^2}{4nB} \right] \tanh \left[\left(E + \sum_{m=2}^{\infty} \alpha_m E^m \right) / kT \right] dE. \quad (10)$$

In the linear case ($\alpha_m = 0$) Eq.(10) transforms into that derived in⁷. It is seen that order parameter is self-consistently expressed through itself and is the function of temperature, dipoles concentrations and nonlinearity coefficients.

Further simplifications of Eq. (10) are possible on sym-

metry grounds. Namely, for the lattice with the center of inversion in paraelectric phase, the order parameter has to be an odd function of electric field, i.e. m 's in Eq.(10) are odd numbers. Conserving only the first nonlinear term in tanh argument, we obtain

$$L = \frac{1}{2\sqrt{\pi nB}} \int_{-\infty}^{\infty} \exp \left[-\frac{(E - E_0 L)^2}{4nB} \right] \tanh \left[(E + \alpha_3 E^3) / kT \right] dE. \quad (11)$$

It is now instructive to consider the mean field limit of equation (11). This limit corresponds to the case of an ordered ferroelectric, where the distribution function of random fields degenerates into a delta function $\delta(E - E_0 L)$. Formally, in our method this limit corresponds to $nr_c^3 \rightarrow \infty$. Substitution of this δ -function into (11) gives the desired mean field equation for order parameter

$$L_{mf} = \tanh \left[\frac{T_{cmf}}{T} (L_{mf} + \alpha_0 L_{mf}^3) \right] \quad (12)$$

where $E_0 = kT_{cmf}$, T_{cmf} is transition temperature in a mean field approximation (see below), $\alpha_0 \equiv \alpha_3 E_0^2$ so that α_0 is dimensionless. We now use the Eq. (11) to derive the equation for ferroelectric phase transition temperature beyond the mean field approximation.

C. Ferroelectric phase transition temperature

The phase transition temperature is defined as a temperature when a nonzero order parameter L appears. In other words, to get an equation for T_c from (11), we should put in it $L \rightarrow 0$. This is accomplished by noting that at small L

$$\exp \left[-\frac{(E - E_0 L)^2}{4nB} \right] \approx e^{-\frac{E^2}{4nB}} \left(1 + \frac{E E_0 L}{2nB} \right). \quad (13)$$

Subsequent substitution of (13) into (11) yields after some algebra

$$\frac{\lambda}{\tau_c} \int_0^{\infty} \frac{(1 + 3\alpha_0 x^2) e^{-\frac{\pi}{4} x^2 \lambda^2}}{\cosh^2 \frac{x + \alpha_0 x^3}{\tau_c}} dx = 1. \quad (14)$$

Here we introduced the following dimensionless variables

$$\lambda = \frac{E_0}{\pi nB} \equiv \sqrt{15nr_c^3}, \quad x = \frac{E}{E_0}, \quad \tau_c = \frac{kT_c}{E_0} \equiv \frac{T_c}{T_{cmf}}. \quad (15)$$

Equation (14) is the main theoretical result of this work. It predicts the existence of the critical concentration of dipoles

$$n_{cr} r_c^3 = \frac{\lambda_{cr}^2}{15},$$

such that for $n < n_{cr}$, the long range order in the system would never be realized. Thus, the critical concentration is determined from the condition, that $\lambda = \lambda_{cr}$ at $\tau_c = 0$. Taking the limit $\tau_c \rightarrow 0^{17}$ in Eq. (14), we obtain $\lambda_{cr} = 1$, which justifies the choice of dimensionless parameter λ . It is seen that the critical concentration does not depend on the coefficient of nonlinearity and it is completely the same as in linear case (see^{7,11}).

Now we demonstrate that in a mean field approximation $\tau_{cmf} = 1$, i.e. that $E_0 = kT_{cmf}$. For that we notice that this approximation corresponds to $\lambda \rightarrow \infty$ in (14), which after some transformations¹⁷ gives $\tau_{cmf} = 1$. This

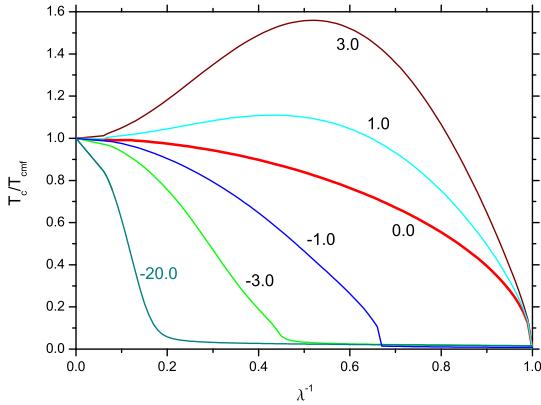


FIG. 1: Theoretical dependence $\tau_c(\lambda^{-1})$. Numbers near curves denote magnitudes of non-linear coefficient, α_0 .

value also does not depend on the coefficient of nonlinearity.

The plot of dependence $\tau_c(\lambda^{-1})$ at different α_0 is shown on the Fig.1. It is seen that at $\alpha_0 > 0$ the dependence $\tau_c(\lambda^{-1})$ has maximum, while at $\alpha_0 < 0$ it does not. Moreover, for negative nonlinearity there is sharp lowering (but not to zero) of τ_c at certain λ^{-1} . This demonstrates that a negative feedback almost destroys long-range order especially at small dipoles concentrations. This behavior shows that at $\alpha_0 > 0$ nonlinear effects produce positive feedback thus enhancing the long-range order in the system, while $\alpha_0 < 0$ the feedback is negative so that long-range order is inhibited but not completely destroyed even for large negative α_0 , see curve for $\alpha_0 = -20$ on the Fig.1. Also, at sufficiently large positive α_0 we can achieve very large enhancement of T_c as compared to its mean field value (see curve for $\alpha_0 = 3$ on the Fig.1). Since in our model we suppose that the value of T_{cmf} is equivalent to T_c for pure PbTiO_3 (the end member of compound), we conclude that large positive α_0 give substantial increase of T_c as compared to the end members of ferroelectric compound.

III. COMPARISON WITH THE EXPERIMENT. DISCUSSION.

In our model, the ferroelectric compounds are considered as an ensemble of electric dipoles embedded in some virtual paraelectric host, its nature we will discuss later. It can be supposed that in the considered system $(\text{BiScO}_3)_{1-x}(\text{PbTiO}_3)_x$ electric dipoles are originated from PbTiO_3 , i.e. their number increase with x increasing. The nondipolar random field sources like point charges, elastic dipoles etc. are also present in such compositions due to the mixed valency of Bi and the difference in charges and ionic radii of Bi^{3+} and Pb^{2+} , Ti^{4+} and Sc^{3+} . These defects could easily be incorporated in the consideration (see¹¹ for details), but we do not con-

sider their contribution here to have the minimal number of adjustable parameters when fitting the theory with experiment.

For quantitative description of experiment in above ferroelectric compounds in the framework of our random field theory (in linear or nonlinear approximation) we should have precise information about the concentrations of electric dipoles and other random fields sources as well as the parameters ε_0 , r_c etc. Unfortunately the available data are strongly restricted for above compounds. That's why we recalculated our dimensionless parameters (15) from the best fit to the experiment². Namely, from the position and "amplitude" of maximum of experimental curve $T_c(x)$ we determine our nonlinearity coefficient $\alpha_0 = 0.81$ and coefficient of recalculation of parameter λ into x . Latter coefficient gives us value $T_{cmf} = 490^\circ\text{C}$ and critical content of PbTiO_3 $x_{cr} = 32\%$. The result of such fitting is shown on the Fig.2.

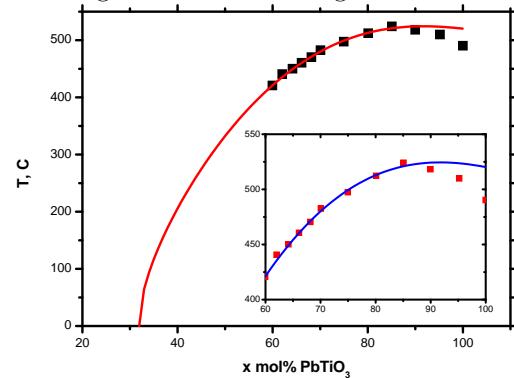


FIG. 2: Comparison of our theory (line) with experiment² (squares). Inset shows the fit in more details.

It is seen in Figure 2 that there is pretty good coincidence between theory and experiment. This coincidence shows, that physical mechanism of enhancement of ferroelectric phase transition temperature beyond the end members in the ferroelectric compounds is the enhancement of initial (i.e. that of end members) long range ferroelectric order in them caused by positive feedback generated by the nonlinear effects with positive coefficient. The obtained value $T_{cmf} = 490^\circ\text{C}$ is very close to transition temperature of PbTiO_3 . This speaks in favour of statement that PbTiO_3 paraelectric phase can be considered as a host lattice.

As we have mentioned above, the origin of nonlinear effects in compound ferroelectrics is quite naturally related to its intrinsic nonlinearities, reflected, for instance, in their hysteresis loop. The physical origin of these nonlinearities may be the nonlinear coupling of the ions in the unit cell as well as the clusterization of dipoles in diluted ferroelectric compounds. Each cluster has its own mesoscopic dipole moment (polarization of cluster) and such clusters can interact between each other. If interaction between such clusters is of positive sign, which may be manifested in the almost rectangular shape of hysteresis

loop, we have the positive feedback with enhancement of initial (i.e. that of end member) long-range order with positive nonlinear coefficient. If the interaction is of negative sign, we have negative feedback and inhibition of ferroelectric order. But such negative feedback cannot destroy ferroelectricity completely, probably except for the case of extremely small dipoles concentration. So, to achieve high positive values of nonlinear coefficients (which are necessary to strongly enhance T_c), we should have (or prepare) the end members of ferroelectric compound with "as much as possible rectangular" hysteresis loop. The contribution of nonlinearities to dielectric response and hysteresis loop in mixed perovskites PZT with impurities was discussed in Ref.¹⁸. The essential role of nonlinearity effect in explanation of phase diagram peculiarities in mixed ferroelectrics $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$,

$\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ and mixed systems of ferroelectric relaxors was shown recently in Ref.¹⁹ and Ref.²⁰ respectively.

To make more precise prediction of which components in ferroelectric compound to use to increase T_c beyond end members value, the measurements of correlation radius, Lorentz factor and ions shifts in both end members and entire above ferroelectric compounds are highly desirable.

It should be finally noted, that the theory outlined here permits one to calculate not only T_c for above substances but virtually any equilibrium and/or nonequilibrium thermodynamic characteristics such as static and dynamic dielectric susceptibility, specific heat etc as a functions of PbTiO_3 content, temperature, electric field and other external parameters.

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